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(54) Dispersion process for ceramic green body.

(57) A process is described for the preparation of a ceramic green body by hydrolyzing two groups of alkoxides to form a dispersion of their reaction product, concentrating the dispersion to a sediment without drying it, and admixing a binder solution, plasticizer and optional release agent with the sediment to make a ceramic slip. The slip is then cast as a ceramic green body. The proportions of alkoxides can be adjusted, when desired, to produce a ceramic green body which is dielectric and useful for microcapacitors or as a conductor.

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DISPERSION PROCESS FOR CERAMIC GREEN BODY

The present invention concerns a process for making a ceramic green body, and has particular though not exclusive application in the field of such green bodies which may be fired into a thin ceramic sheet or tape for use in a multilayer capacitor or as a conductor.

A multilayer capacitor is a stack of a number of ceramic capacitor sheets connected in parallel to produce a capacitor of high total capacitance. These capacitors may be very small, and typically comprise between 40 and 50 ceramic sheets, each about 20 μm thick. The entire capacitor may be only about 1 mm thick. These devices find many uses in microcircuitry.

However, there is a need for even thinner ceramic sheets or bodies, within the range of 3 to 10 μm in thickness. This is due to the fact that equivalent capacitance could thereby be achieved using only half as many of these thinner sheets, since capacitance is inversely proportional to the thickness of the ceramic sheet. The reduction in the number of sheets would then result in a savings in material costs, because the electrode layers interspersed between the ceramic layers in a capacitor are made of expensive noble metals, and with fewer, thinner sheets, fewer electrode layers would be required. In the past it has been very difficult to make sheets of this reduced thickness because current commercial methods of producing the green (unfired) sheets, also called tapes, involve processing of solids, including ceramic powders.

These ceramic powders, which are dielectric and/or conductive, are generally dispersed into an organic solvent such as a methyl ethyl ketone/ethanol mixture. The powders are often barium titanate admixed with other compounds such as strontium titanate, lead titanate, calcium zirconate, lead oxide, borates and silicates. Ball-milling is generally necessary to maximize dispersion in the solvent, and often requires several hours at a minimum. The dispersed powders are then mixed with polymeric organic binders, plasticizers and surfactants to form a slip, which is tape-cast onto a nonporous substrate and dried in an oven to form a flexible "green tape."

To produce a capacitor, this green tape or green body is screen-printed with a noble metal electrode ink. Forty or fifty layers, typically, of the printed tape are then laminated and, after dicing into chips or sheets, fired to burn off the organic binder. The inorganic chips are sintered at high temperatures, typically between 1000 and 1400°C, to densify the sheets and improve their strength and conductivity. The result is a mechanically and

electrically acceptable device.

A problem very commonly faced in this process, however, that tends to militate against reducing the thickness of the sheets or tapes beyond thicknesses currently being produced, is the fact that ceramic powders are usually agglomerated when received and remain so to some extent even after lengthy ball-milling prior to and after dispersion in a solvent. This agglomeration makes it difficult to produce sheets of only 3 to 10 μm in thickness that are of uniform quality, since the size and shape of the initial ceramic particles are critical factors in producing a good quality final product. This process also tends to produce sheets that exhibit loading levels that are less than optimal, and the reduced density increases the degree of shrinkage of the tape during firing. Ideally, the particles should be uniformly sized and equiaxially shaped, and should also demonstrate high purity.

Therefore, because of the problems associated with the ceramic powders and their general unsuitability to producing the thinner ceramic sheets or tapes now sought, it would be desirable to have a ceramic green body prepared from a slip formulation which does not generally require ball-milling or other milling steps at any point and for which powder agglomeration does not present a significant problem, which exhibits good ceramic loading levels, and which therefore does not generally require processing of dry ceramic powders, with the accompanying quality problems and thickness limitations that such processing entails. The present disclosure describes such an invention and involves an *in situ* finely dispersed slurry that may be used to produce a ceramic green body.

Accordingly, there is provided a process comprising (a) forming a hydrolyzable solution of at least one compound characterized as $A(\text{OR})_x$, wherein A is at least one of the metals Be, Mg, Ca, Sr, Ba, Ge, Pd, Nd, Y, La, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sb or Bi; at least one compound characterized as $B(\text{OR})_x$, wherein B is at least one of the metals Ti, Zr, Sc, Y, La, Nb, Fe, Ta, W, Mn, Sn, Mg, Cu, Ni, Co, Mo or Zn, and wherein R is a group characterized as C_yH_z wherein y is an integer from 1 to 10, z is an integer y, 2y, 2y + 1 or 2y - 1; and x is an integer from 1 to 7, such that the compounds of formula $A(\text{OR})_x$ and $B(\text{OR})_x$ are suitable to be hydrolyzed to form a compound characterized as $\text{ABO}_{3-\Delta}$ wherein Δ is a number from 0 to 1.33, and an alcohol suitable to dissolve said compounds $A(\text{OR})_x$ and $B(\text{OR})_x$; (b) hydrolyzing said hydrolyzable solution to form a hydrolyzed dispersion of this compound characterized as $\text{ABO}_{3-\Delta}$ in the alcohol; (c) concentrating at

least a portion of the dispersion to a sediment; (d) admixing a binder solution, a plasticizer, and optionally a release agent with the sediment to make a ceramic slip formulation; and (e) preparing a ceramic green body from this slip formulation.

The process of the present invention can be advantageously used to prepare a ceramic green body from a solution without the need to use ceramic powders. The term "ceramic green body" refers to a body, often a tape or sheet, of a material that can be converted into a ceramic upon firing.

The admixture and hydrolysis of soluble metal compounds of the formula $A(OR)_x$ and $B(OR)_x$ of the appropriate stoichiometry can lead to the formation of metal oxides that have desirable properties including both insulation and conductivity.

The starting components to be utilized here typically comprise at least one compound of the formula $A(OR)_x$ and at least one compound of the formula $B(OR)_x$, each of which is generally an alkoxide, which are hydrolyzed together and used in forming a hydrolyzed dispersion in alcohol, with which is then admixed at varying points a binder solution, a plasticizer and optionally a release agent. The alcohol and two groups of alkoxides form what is referred to as the "hydrolyzable solution," before hydrolysis, and afterward is referred to as the "hydrolyzed dispersion." The amounts for each of the components of the present invention have been calculated based on either the hydrolyzable solution or the hydrolyzed dispersion. The alcohol generally comprises from 30 to 99 percent by weight of the hydrolyzable solution, and preferably from 90 to 98 percent by weight. The alcohol is preferably selected to minimize, and more preferably avoid, the formation of insoluble alkoxide components through metathetical reactions during the herein disclosed process. Among the preferred alcohols are isopropanol, butanol, sec-butanol, pentanol and isoamyl alcohol. Isopropanol is generally more preferred here.

For the purposes of this invention, the compound of the formula $A(OR)_x$ desirably comprises at least one of the metals Be, Mg, Ca, Sr, Ba, Ge, Pb, Nd, Y, La, Pm, Sm, Sb, Eu, Bi, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu, preferably Be, Mg, Ca, Sr, Ba, Ge, Pb, Y, Sb, La, or Bi, and more preferably Pb, Y, Ca, La, Ba, Mg or Sr. One or more selections from this group of elements is incorporated as A in the alkoxide formula $A(OR)_x$.

The compound of the formula $B(OR)_x$ comprises at least one of the metals Ti, Zr, Sc, Y, La, Nb, F, Ta, W, Mn, Mg, Zn, Cu, Ni, Co, Mo or Sn, preferably Ti, Zr, Sc, Y, La, Nb, W, Sn, Mg, Ta, Cu or Zn, and more preferably Ti, Zr or Cu. Although it is possible to combine only one compound adhering to the formula $A(OR)_x$ with only one compound

adhering to the formula $B(OR)_x$ in the present invention, the two types of compounds will be referred to herein as the first and second groups of alkoxides, respectively, since the formulas represent alkoxides as defined, and groups of each can be utilized at the same time. The first and second groups of alkoxides together represent from 1 to 70 percent by weight of the hydrolyzable solution, and preferably from 2 to 10 percent by weight; the alcohol representing the remainder.

The R in both of the alkoxide formulas $A(OR)_x$ and $B(OR)_x$ represents a compound of the general formula C_yH_z , wherein y is an integer from 1 to 10 and z is an integer y, 2y, 2y + 1 or 2y - 1. The x is an integer from 1 to 7. The two groups of alkoxides are dissolved in the alcohol, and are such that they are suitable to be hydrolyzed to form a compound characterized as $ABO_{3-\Delta}$. Δ is defined as a number from 0 to 1.33, preferably either 0 or from 2/3 to 5/6, depending on the desired end use of the ceramic green body. It is important to note that one or both of these two groups of alkoxides may comprise mixtures of compounds employing the designated elements.

The hydrolysis of the two groups of alkoxides together is preferred and is accomplished by the addition of a greater than stoichiometric amount of water while heating at reflux temperature. This means that the amount of water to be added is preferably from 0.5 to 70 percent by weight of the hydrolyzable solution, and more preferably from 0.5 to 3.5 percent. In general, this heating should be of sufficient time and temperature to substantially hydrolyze the solution, and is preferably done for at least 1 hour with continued stirring. Alkoxide solutions refluxing within the range of 70 to 110 °C are preferred when the alkoxides chosen include barium and titanium because hydrolysis within this temperature range results in the formation of crystallites of $BaTiO_3$ having small, substantially uniform particle size in the 100 to 2000 Å range. Even more preferred are solutions refluxing within the range of 80 to 90 °C. Refluxing may be continued as long as desired, but a time within the range of 1/2 hour to 5 hours is preferred, and 1/2 hour to 1 1/2 hours is more preferred, from a standpoint of yield as well as convenience and commercial practicability.

The water is added preferably in an alcohol solution, preferably within the range of 10 to 50 percent water. The water and alcohol should be miscible at whatever percent mixed, and again the alcohol for this hydrolysis is preferably selected to minimize, the more preferably to avoid, the formation of insoluble alkoxide components through metathetical reactions. The rate of addition is useful in determining the desired small particle size and reducing the possibility of undesirable agglomer-

ation. It is preferable to use a rate within the range of 0.2 to 0.4 cubic centimeter per minute (cc/min), more preferably 0.3 to 0.35 cc/min. This latter rate helps produce particles in the 100 to 300 Å range. These absolute rates may be, equivalent to for example, from 0.13 to 0.26 percent per minute, preferably from 0.2 to 0.23 percent per minute, or may be equivalent to from 0.08 to 0.16, preferably from 0.12 to 0.14 percent per minute. It is possible to increase the addition rate once an approximately stoichiometric amount of water has been added. If the water is added too rapidly at the start, however, agglomerates may form.

The hydrolysis step results in the conversion of the coordination compound formed by the first and second groups of alkoxides in the alcohol to a dispersion of the compound characterized as $ABO_3 \cdot \Delta$. $ABO_3 \cdot \Delta$ preferably comprises combinations of $BaTiO_3$ and from 2 to 20 mol percent of such others of the same characterization as $CaZrO_3$, $BaZrO_3$, $PbTiO_3$ and $SrTiO_3$. Other possibilities here include, for example, $CaTiO_3$, $MgTiO_3$, $SrZrO_3$, $BaYCuO_3$, $Ba_{23}Y_{13}CuO_{73}$ and related compounds in which any of the designated alkoxide elements is present.

It should be noted that the $ABO_3 \cdot \Delta$ system, which is the hydrolyzed dispersion, ideally displays a small particle size along with a narrow size distribution and substantial uniformity of stoichiometry between the first and second groups of alkoxides. It is preferable to use substantially stoichiometric proportions of these two groups of alkoxides to produce a body exhibiting significant dielectric characteristics. A preferred range is a ratio between the two groups of alkoxides of 1.1 to 1, more preferably 1.05 to 1, and most preferably 1.01 to 1. If dielectric properties are not of importance to a desired application, the proportionality is correspondingly less important. The small and uniform particle size helps to ensure uniform sintering and reduces the likelihood of flaws in the final ceramic green body.

Following the hydrolysis, it is optional to remove the excess water remaining in a separate step. For this, an azeotropic distillation, for example, may be done so that a substantially dry alcoholic slurry results. Residual water may still be left and will not affect the final outcome as long as the water content is sufficiently low so as not to create binder solubility problems. Other drying methods including, for example, the use of drying agents such as 1,2-dimethoxy-propane, may alternatively be employed. This step is not per se necessary, however, since the subsequent concentration step, described below, serves to minimize the amount of water remaining in the final slip formulation.

A dispersant may be added at this point, in the

amount of preferably from 0.002 to 0.5 percent by weight of the hydrolyzed dispersion, and more preferably 0.008 to 0.05 percent by weight. It is alternatively possible to add it to the original alkoxide solution prior to hydrolysis, or to the hydrolyzed dispersion prior to the drying step; however, if drying is done by distillation, a substantial loss of the dispersant may result, which may in turn allow greater agglomeration afterward. Among possible dispersants are, for example, anionic dispersants such as amine salts of alkylaryl sulfonate, ethanol, polyacrylate, polymethacrylate or menhaden fish oil. Ethanol and amine salts of alkylaryl sulfonate are preferred here, and since ethanol may also be chosen as the alcohol for the original dispersion's formation, a separate dispersant addition may be thereby obviated. The dispersant serves to increase the uniformity and reduce the agglomeration of the $ABO_3 \cdot \Delta$ dispersion.

While the present invention is not limited to a strict order of steps in all respects, obvious limitations will apply in order to produce a mechanically and electrically acceptable device. One step generally occurring after the hydrolysis is the concentration of the disperse, or internal, phase to a nonisolated sediment in a greatly reduced volume of the continuous, or external, phase. The remaining volume of the continuous phase, which is primarily alcohol, is ideally just sufficient to maintain the $ABO_3 \cdot \Delta$ dispersion in a nonagglomerated state. Experimentally, this dispersion was determined essentially visually. The amount of continuous phase remaining may be determined, for example, by measuring either the volume of distillate collected during the drying/concentration step or the liquid content of the sedimentation volume following gravimetric settling or centrifugation.

Centrifugation provides one effective means of concentration without complete isolation from the continuous phase and is the preferred method. Other means may include distillation, decantation (gravitational sedimentation), or combinations of these procedures. Complete isolation, i.e., drying of the sediment, at any point should be avoided both because of the undesirable agglomeration that will result and because of the difficulty of redispersing the formulation if it has dried. An important point of this invention, as already noted, is that the formulation remains a slurry throughout the processing.

Another important point to the present invention is that it employs a binder solution. The binder serves to help disperse the solids and to stabilize the suspension, and also provides integrity and strength to the final product. If concentration is by distillation, the binder solution may be added prior to concentration, provided that the dispersion, or suspension, is sufficiently water-free. However, in all cases, and especially in the cases of concentra-

tion by centrifugation and by gravitational settling, addition of the binder solution after concentration minimizes the loss of binder in the discarded external phase.

The solvent employed for the binder can be aqueous or nonaqueous, with the solvent choice obviously depending on the binder choice. Examples of possible solvents include toluene, methyl ethyl ketone, methanol or a methanol/water mixture, with toluene being preferred. If an organic-based system is chosen, ethylcellulose make an excellent binder. Other organic binder systems are those using ethyl hydroxyethyl cellulose and polyacrylic acid esters. For a water-based system, polymers such as methylcellulose, hydroxypropyl ethylcellulose, hydroxybutyl methylcellulose, carboxymethylcellulose, hydroxyethylcellulose, polyvinylalcohols, polyvinylpyrrolidones, poly(acrylic acid), polyacrylamide, polyethylene oxides and mixtures of these polymers can be employed as binders in formulating the slip. The cellulose ethers are preferred binders, and more preferred here is water-soluble methylcellulose. Obviously, an aqueous binder system obviates the need to substantially remove water from the hydrolyzed dispersion.

The use of these and related binders will help to form a very uniform slip that upon casting forms a thin transparent film, indicating good uniformity of metal oxide particulates and binder particulates. The particulates range from 100 to 2000 Å in size. The binder solvent represents preferably from 1 to 6 percent by weight of the hydrolyzed dispersion, and more preferably from 2 to 4 percent by weight. The binder itself is preferably from 0.1 to 5 percent by weight, and more preferably from 0.1 to 1 percent by weight.

A release agent, such as a polyol or mineral oil, optionally may also be added to the binder solution prior to adding the solution to the dispersion. This serves to facilitate easy stripping of the green tape from the casting substrate. When using a glass substrate, 1,2,4-butanetriol makes an excellent release agent. Nonglass substrates, such as polypropylene, may also be used while employing other release agents. The release agent preferably amounts from 0.01 to 5 percent by weight of the hydrolyzed dispersion, and more preferably from 0.05 to 3 percent by weight.

In the present invention, a plasticizer is also employed and serves to lower the glass transition point of the binder to ambient or room temperature to increase the flexibility of the film, thereby making the green body or tape more easily removed from the substrate and more suitable for lamination. Examples of typical plasticizers include dimethyl formamide and propylene glycol, both of which are particularly effective in a methylcellulose aqueous solution, and dioctyl phthalate and benzyl butyl

phthalate, both of which work well in an ethylcellulose organic-based system. For an ethylcellulose binder solution, dioctyl phthalate and benzyl butyl phthalate are preferred plasticizers. The plasticizer is added preferably in an amount of from 0.01 to 5 percent by weight of the hydrolyzed dispersion, and more preferably from 0.05 to 3 percent by weight.

It is important when adding the binder solution containing the plasticizer and release agent to the $\text{ABO}_{3-\Delta}$ dispersion to use some means to keep the viscosity of the dispersion as low as possible. This should be done both during and after the addition of the binder. Means such as the use of appropriate commercially available surfactants may be employed when necessary to avoid agglomeration.

The final component of the slip formulation is optionally one or more sintering aids. For these, low-melting eutectic oxide mixtures may be employed, including compounds such as GeO_2 , B_2O_3 , PbO , Bi_2O_3 , TiO_2 , Sb_2O_3 , SnO , and SiO_2 , preferably GeO_2 , B_2O_3 , PbO , Bi_2O_3 , Sb_2O_3 , and SnO . There are various ways in which one or more of these can be added so that they can perform their function of densifying the ceramic film and thereby increasing its strength and dielectric properties. In one preferred embodiment a third group of alkoxides of a type that will form sintering aids, such as glass frits, upon hydrolysis is selected. This group is then hydrolyzed in alcohol either concurrently with the first and second groups of alkoxides, in a step-wise fashion before or after the hydrolysis of the first and second groups, or entirely separately from the first and second groups. In the latter case the eutectic oxide mixture may be added at any subsequent point in the process of the present invention, such as prior to or after concentration or along with the addition of binder solution, plasticizer, release agent and so forth. Alternatively, the sintering aid to be employed may be purchased commercially, obviating the need for hydrolyzing a third group of alkoxides. The amount used represents from 0.01 to 2 percent by weight of the hydrolyzed dispersion, and preferably from 0.03 to 0.2 percent by weight. To further augment the dielectric properties of the final film, dopants that will form MnO , Mn_2O_3 , CoO , or Co_2O_3 may also be added, but they are not necessary to the present invention.

The last step of this process involves the conversion of the uniform concentrated dispersion into a ceramic green body using known methods, such as curtain-coating, tape-casting or doctor-blading. It is preferred to tape-cast a single layer of the non-isolated dispersion sediment onto a nonporous substrate. The techniques for converting slip formulations into flexible green tapes are well known. For example, see the chapter "Tape-Casting of

Ceramics" in Ceramic Processing Before Firing, edited by G. Y. Onada, Jr. and L. L. Hench, John Wiley and Sons, Inc., N. Y. (1978), pp. 411-447.

The green body prepared according to the process of the present invention can then be converted using known methods into a thin ceramic sheet or tape. Typically, the green body is calcined to burn off the polymer and to convert the tape or sheet to a ceramic material. This is then sintered, or fired, at a temperature of from 1000 to 1400° C. Advantageously, the green body of the present invention exhibits a good loading level which tends to reduce shrinkage upon firing. Preferably, the fired ceramic sheets, which may also be called films, of the present invention range from 1 to 50 μm in thickness, more preferably from 3 to 10 μm . They can be employed in the preparation of capacitors or conductors which have a reduced volume compared to many known capacitors or conductors due to the increased capacitance of the thinner sheets. Thus, these capacitors may be less expensive to produce than many known capacitors because they require fewer noble metal electrode layers.

It should be noted that steps necessary to the present invention, regardless of order taken, include the preparation of a hydrolyzed dispersion of the first and second groups of alkoxides, provided hydrolysis of these two groups occurs together, the concentration of the dispersion, and the addition of binder solution, plasticizer and release agent to make a slip formulation to be used in preparing a ceramic green body. The order of addition of the binder solution, plasticizer and optional release agent may be varied. As noted, for example, the binder solution, plasticizer and optional release agent, or any combination thereof, may be added prior to the concentration, although it is preferable to add these after the concentration to minimize their loss in any discarded external phase. The optional dispersant cannot be added before the hydrolysis, but may be added either before or after an optional drying step. Hydrolysis itself may be done in more than one step, with a third group of alkoxides hydrolyzed in order to supply the optional sintering aids, and then the first and second groups of alkoxides added for a second hydrolysis, for example, or in reverse order. Other variations in order are also possible, including having more than one addition step for a given component, as long as the weight percent ranges are satisfied. As noted, commercial sintering aids may alternatively be used and dispersed at various points in the process.

The following examples are given to illustrate the present invention and are not intended to be, nor should they be construed as being, limitative in any way of the scope of the invention. All parts and

percentages are by weight unless otherwise indicated.

Example 1

About 6.2 g (0.0218 mole) of titanium isopropoxide $[\text{Ti}(\text{i-C}_3\text{H}_7\text{O})_4]$, 6.8 g (0.0215 mole) of barium isopropoxide isopropylate $[\text{Ba}(\text{i-C}_3\text{H}_7\text{O})_2\text{C}_3\text{H}_7\text{OH}]$, and 150 ml of isopropanol were added to a 500 ml Schlenk flask in a dry box. The admixture was refluxed over argon for 30 minutes to produce a colorless solution.

A solution of 5 ml water and 5 ml isopropanol was then added to the refluxing solution at the rate of about 0.2 ml/min. The water/isopropanol solution had been degassed previously. The addition was made via a 1/16" (0.16 cm) cannular tube and the solution was continually stirred during the addition. At this point the reaction mix showed a dispersion of finely divided white particles. Refluxing was continued for about 2 hours, and the solution allowed to cool naturally.

The final product, a milky dispersion, was then allowed to sit in a graduated cylinder at room temperature. There was produced a gravitational sediment volume of 25 ml in which was estimated to be about 3.2 g of BaTiO_3 .

The XRD (x-ray diffraction) pattern of the settled BaTiO_3 showed as average crystallite diameter of 110 Å which would correspond to a surface area of 91 m^2/g . TEM (Transmission Electron Microscopy) showed primary particles (spheres) measuring about 185 Å in diameter.

To a mechanically stirred gravitational sediment volume of this BaTiO_3 (3.2 g/25 cc) prepared in the above manner was added dioctyl phthalate, 0.3 g, as a plasticizer, and 1,2,4-butanetriol, 0.3 g, as a release agent. This dispersion was stirred at 300 rpm for 10 minutes and 0.8 g of ETHOCEL* 45 brand ethylcellulose was added over a 30 minute period, as a binder. (ETHOCEL is a trademark of The Dow Chemical Company.) Stirring was then continued an additional 1.5 hours. One ml of a 0.6 percent by weight solution of an amine salt of alkylaryl sulfonate in isopropanol was then added as a dispersant.

An 8.0 mil thick film was cast on glass using a doctor-blade. The film was dried at room temperature in air to produce a translucent 0.7 mil film that was easily stripped from the glass surface. X-ray powder diffraction line broadening measurements of this film showed an average crystallite size of 133 Å. STEM (Scanning Transmission Electron Microscopy) photos showed slightly agglomerated particles with an average primary particle diameter of 200 Å. Thermogravimetric analysis of the film gave a ceramic content of the film of about 67

percent by weight.

Example 2

Ba(i-C₃H₇O)₂ (4.63 g, 0.0182 mole), Sr(i-C₃H₇O)₂ (0.71 g, 0.0034 mole), Ti(i-C₃H₇O)₄ (5.92 g, 95 percent in isopropanol, 0.0197 mole), Zr(n-C₃H₇O)₄ (0.75 g, 95 percent in isopropanol, 0.0022 mole) and Pb(i-C₃H₇O)₂ (0.14 g, 4.3 x 10⁻³ mole) were dissolved in 250 ml of dried and deoxygenated isopropanol. The solution was added to a stirred reaction vessel under an inert atmosphere and refluxed for about 45 minutes. A 10 percent by volume solution of distilled water in isopropanol, as a solvent, was added at a rate of about 0.3 ml/min, until a volume of 35 ml was added. The addition rate was then increased to 3 ml/min until a total volume of 100 ml had been delivered. Reflux was continued an additional 1.5 hours during which hydrolysis was substantially completed.

The water was removed by azeotropic distillation and the suspension was then concentrated by centrifuging at 40 G until a bed volume of 25 ml was obtained. The nonisolated product was estimated to weigh about 5 g and analysis showed it to have the nominal composition: BaTiO₃, 71.77 percent; SrTiO₃, 12.23 percent; BaZrO₃, 11.56 percent; TiO₂, 0.58 percent; and PbO, 3.85 percent.

ETHOCEL 45 ethylcellulose, 1 g, was dissolved in 10 ml of toluene and 1 ml of ethanol, and 0.3 g of dioctyl phthalate and 0.7 g of propylene glycol were added. The solution was then added to the centrifugate and the mixture stirred for about 2 hours. The resultant slip had a viscosity of about 400 centipoise. The slip was then cast by doctor-blade at 5 and 10 mil thicknesses, resulting in transparent dried films of 0.7 to 1.5 mil thicknesses, respectively. Laminates of 10 layers of the films pressed at 250 °C and 1500 psi were translucent and had a ceramic content of about 71.5 weight percent.

Example 3

Ethanol/isopropanol (5 ml/300 ml) was placed in a 500 ml Schlenk flask which was attached to a Soxhlet extraction system. The set-up was degassed and pressurized with argon three times. While under a positive pressure of argon, there was placed into the Soxhlet chamber a glass thimble with 10 g (0.25 mole) of 99.5 percent calcium granules.

Refluxing of the ethanol/isopropanol was commenced under a blanket of argon. The reaction was not vigorous. The system was vented slightly for the escape of generated hydrogen. After refluxing

for 1 week, there remained in the glass thimble a considerable amount of greyish-white powder, believed to be CaO (hydrolysis product of calcium alkoxide). The adventitious water entered the system via the ethanol that was used. In the reaction pot was dispersed a trace amount of the CaO which was filtered off in an inert atmosphere. The filtration was done through a fine glass frit (4-5.5 μ), time about 6 hours. Continuance of drawing a vacuum on the filtrate for about 15 hours produced 27 g of a creme-colored powder.

Analysis (plasma emission) of a 2.5 percent isopropanol solution showed the solid to be Ca-(OCHCH₃)₂ contaminated with about 10 percent Ca(OCH₂CH₂CH₃)₂.

Zirconium n-propoxide propylate (3.81 g), 90 percent calcium isopropoxide (1.64 g), prepared above, and isopropanol (300 ml) were added to a 500-ml Schlenk flask. The mix was refluxed over argon for 30 minutes to give a slightly yellow solution.

To this refluxing solution was added (0.2 ml/min) with stirring a degassed solution of 2.5 ml/2.5 ml H₂O/isopropanol. The addition was added via 1/16 inch (0.16 cm) cannular tube. After the addition (about 1/2 hr) the reaction mixture of finely dispersed white particles continued to be refluxed for 2 hours.

At room temperature the product (a milky dispersion) was allowed to sit in a graduated cylinder. After about 3 days a gravitational sediment volume of 35 ml with 4.4 percent CaZrO₃ was present. On centrifuging the volume was reduced to 14 ml of a 10 percent CaZrO₃ dispersion. A look under the microscope revealed agglomerates as large as 25 μm.

An XRD of the centrifuged sediment calcined to 900 °C for 2 hours produced a pattern showing the presence of CaZrO₃ and ZrO₂. Analysis (plasma emission) showed a Ca/Zr atomic ratio of 1.00/1.14.

The ceramic green body was prepared and slip cast to tape by the procedure of Example 2.

Example 4

BaTiO₃/CaZrO₃ (80/20 weight percent) Slip Formulation

After hand mixing the centrifuged sediment volumes of BaTiO₃/isopropanol (4 g/12 ml) and CaZrO₃/isopropanol (1 g/12 ml), there was added 6 ml of 12.5 percent ETHOCEL 45/isopropanol solution. With continued stirring (about 300 rpm) of the dispersion, there was added dioctylphthalate (0.73 g) and 1,2,4-butan triol (0.73 g). After an additional

30 minutes of stirring, there were added 6 drops of a 0.6 percent solution of the emulsifier in isopropanol. A look at the slip dispersion under a microscope showed a glassy mass of particles of about 2.5 μm with some agglomerates of about 15 μm .

An 8-mil slip was cast and dried at room temperature to give a slightly cloudy film which was unable to be stripped from a glass substrate. It appeared that the film was too brittle. A TGA showed a 66 percent solid ceramic film content. An XRD of the powdered film showed only the BaTiO_3 pattern with an average particle diameter of 116Å (The CaZrO_3 being amorphous did not exhibit an XRD pattern.)

A tablet was pressed out of the powdered film, calcined up to 850°C, and then sintered at 1310°C for 1½ hours. A surface XRD of the sintered tablet showed the presence of $[\text{BaCa}] [\text{TiZr}] \text{O}_3$. STEM photos of both a fracture and surface of the tablet showed some pores, but looked fairly dense overall, estimated at about 85 to 90 percent dense.

Example 5

According to the procedure of Example 2, the following ratios of reactants were admixed in 500 ml of dry and deoxygenated isopropanol, $\text{Ba}(\text{i-C}_3\text{H}_7\text{O})_2$ (9.28 g, 0.0363 mole), $\text{Y}(\text{i-C}_3\text{H}_7\text{O})_3$ (4.84 g, 0.0182 mole), and $\text{Cu}(\text{C}_2\text{H}_5\text{O})_2$ (8.38 g, 0.0546 mole). The solution was stirred and refluxed for 45 minutes at which time the mixture was hydrolyzed as in Example 2. The hydrolysis resulted in the formation of a dispersion of a solid powder having the nominal composition of $\text{Ba}_{2/3}\text{Y}_{1/3}\text{CuO}_{3-\Delta}$, such that $3-\Delta = 2.167$ to 2.33. The dispersion can be concentrated, admixed with a binder solution and a plasticizer to make a slip formulation, and cast as a ceramic green body as described in Example 2. After appropriate firing, the resultant ceramic body has utility as a conductive material.

It should be noted particularly that the invention includes within its scope processes in which B is Ni, Co, or Mo, and processes in which Δ in the formula noted above is non-zero. Also particularly included are processes in which the said compound of the formula $\text{ABO}_{3-\Delta}$ is $\text{Ba}_{2/3}\text{Y}_{1/3}\text{CuO}_{7/3}$.

Claims

1. A process for preparing a ceramic green body comprising:

(a) forming a hydrolyzable solution of at least one compound of the formula A(OR)_x , wherein A is at least one of the metals Be, Mg, Ca, Sr, Ba, Ge, Pb, Nd, Y, La, Pm, Sm, Eu, Gd, Tb, Dy,

Ho, Er, Tm, Yb, Lu, Sb or Bi;

at least one compound of the formula B(OR)_x ,

wherein B is at least one of the metals Ti, Zr, Sc, Y, La, Nb, Fe, Ta, W, Mn, Sn, Mg, Cu, Ni, Co, Mo or Zn,

wherein R is a group of the formula C_yH_z wherein y is from 1 to 10,

z is equal to y, $2y$, $2y + 1$ or $2y - 1$, and

x is from 1 to 7,

such that the compounds of formulas A(OR)_x and B(OR)_x are suitable to be hydrolyzed to form a compound of the formula $\text{ABO}_{3-\Delta}$, wherein Δ is from 0 to 1.33, and an alcohol suitable to dissolve said compounds of the formulas A(OR)_x and B(OR)_x ;

(b) hydrolyzing said hydrolyzable solution to form a hydrolyzed dispersion of said compound of the formula $\text{ABO}_{3-\Delta}$ in said alcohol;

(c) concentrating at least a portion of said dispersion to a sediment;

(d) incorporating in the sediment prior to, during or after the sedimentation a binder solution, a plasticizer, and optionally a release agent, to make a ceramic slip formulation; and

(e) preparing a ceramic green body from said slip formulation.

2. The process of Claim 1 wherein said hydrolyzable solution is hydrolyzed by adding water in an amount from 0.5 to 70 percent by weight of said hydrolyzable solution.

3. The process of Claim 1 or Claim 2 wherein said compound of the formula A(OR)_x and said compound B(OR)_x are hydrolyzed together.

4. The process of any one of the preceding claims wherein the hydrolysis is conducted by adding water to the hydrolyzable solution at a rate from 0.2 to 0.4 cc/min.

5. The process of any one of the preceding claims wherein A is Mg, Ca, Sr, Ba, Y, La, or Pb.

6. The process of any one of the preceding claims wherein B is Ti, Zr, Sc, Y, La, Nb, Ta, W, Sn, Mg, Cu or Zn.

7. The process of any one of the preceding claims wherein said alcohol comprises from 30 to 99 percent by weight of said hydrolyzable solution.

8. The process of any one of the preceding claims wherein said hydrolyzable solution comprises from 1 to 20 percent by weight of compounds of the formulas A(OR)_x and B(OR)_x .

9. The process of any one of the preceding claims wherein from 0.002 to 0.5 percent by weight of a dispersant is admixed with said hydrolyzed dispersion or said sediment.

10. The process of any one of the preceding claims wherein said binder solvent comprises from 1 to 6 percent by weight of said hydrolyzed dispersion.

11. The process of any one of the preceding claims wherein said binder comprises from 0.1 to 5 percent by weight of said hydrolyzed dispersion.

12. The process of any one of the preceding claims wherein said plasticizer comprises from 0.01 to 5 percent by weight of said hydrolyzed dispersion.

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13. The process of any one of the preceding claims wherein said release agent comprises from 0.01 to 5 percent by weight of said hydrolyzed dispersion.

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14. The process of any one of the preceding claims wherein said release agent is 1,2,4-butanetriol.

15. The process of any one of the preceding claims wherein said hydrolyzed dispersion comprises excess water.

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16. The process of Claim 15 wherein said excess water is substantially removed prior to admixing said binder solution.

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17. The process of any one of the preceding claims wherein said slip formulation comprises a sintering aid.

18. The process of any one of the preceding claims wherein said ceramic green body is a sheet within the range of 1 to 50 μm in thickness.

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19. A ceramic material produced by firing a green body produced by a process as claimed in any one of the preceding claims.

20. A capacitor or electrical conductor comprising a ceramic material as claimed in Claim 19.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 87 31 0463

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X,P	US-A-4 710 227 (A.D. HARLEY et al.) * whole document *	1-20	C 04 B 35/00
X	EP-A-0 125 507 (KANEKAFUCHI KAGAKU KOGYO K.K.) * claims 1, 6, 10, 16; page 6, line 3 - page 7, line 29; page 13, line 24 - page 15, line 19; page 19, line 9 - page 20, line 34; examples 1-4 *	1,3,5-8 ,19,20	
A		2,17,18	
A	US-A-4 561 872 (J.C. LUONG et al.) * claim 1; column 2, lines 12-55; column 4, lines 18-27; example VI *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 01 G 1/02 C 04 B 35/00
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 23-02-1988	Examiner STROUD J.G.
CATEGORY OF CITED DOCUMENTS			
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